

Role of Vibrational Spectroscopy at the
U.S. Environmental Protection Agency's
Environmental Research Laboratory in
Athens, Georgia

(U.S.) Environmental Research Lab., Athens, GA

1988



U.S. Department of Commerce
National Technical Information Service

NTIS

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/M-88/021	2.	3. R PB89-130439
4. TITLE AND SUBTITLE ROLE OF VIBRATIONAL SPECTROSCOPY AT THE U.S. ENVIRONMENTAL PROTECTION AGENCY'S ENVIRONMENTAL RESEARCH LABORATORY IN ATHENS, GEORGIA	5. REPORT DATE 1988	
7. AUTHOR(S) Timothy W. Collette	6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory U.S. Environmental Protection Agency Athens, Georgia 30613	8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory - Athens, GA Office of Research and Development U.S. Environmental Protection Agency Athens, Georgia 30613	10. PROGRAM ELEMENT NO. ANWBLE	
	11. CONTRACT/GRANT NO.	
	13. TYPE OF REPORT AND PERIOD COVERED	
	14. SPONSORING AGENCY CODE EPA/600/01	
15. SUPPLEMENTARY NOTES Applied Spectroscopy 42(6):1139-1142, August 1988		
16. ABSTRACT The Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens GA, is best known by vibrational spectroscopists as the laboratory where much of the pioneering work on the development of a sensitive, real-time gas chromatograph/Fourier transform infrared system was conducted. Current work in vibrational spectroscopy involves two applications. One area involves the identification of unlisted pollutants--a conventional but somewhat specialized, usage. The second area, a more novel application of vibrational spectroscopy and one for which few related studies have been reported, involves the prediction of environmental fate constants for chemicals.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 6
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE DCA/0.95/26.95

(AERL) is best known by vibrational spectroscopists as the laboratory where much of the pioneering work on the development of a sensitive, real-time GC/FT-IR system was conducted. In addition to the conception of the gold-coated light pipe, upon which essentially all commercially available GC/FT-IR interfaces are based, the early work on GC/FT-IR at this laboratory is credited with creating much of the enthusiasm that was responsible for a concerted effort by numerous researchers to develop the technique to its current level of sophistication. This innovative work has earned the man responsible for it, Dr. Leo V. Azarraga (a research chemist at AERL), recognition as the "Father of Modern GC/FT-IR."

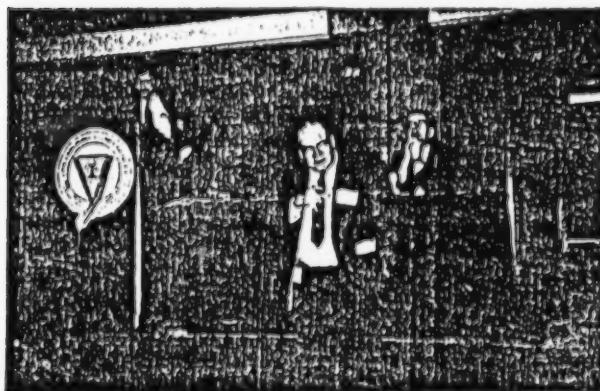
Over the years, the objectives of AERL have evolved, and although analytical instrument development is not currently being aggressively pursued, vibrational spectroscopy continues to play a substantial role in realizing the laboratory's research mission. AERL conducts fundamental and applied research required to predict and assess the human and environmental exposures and risks associated with conventional and toxic pollutants in water and soil ecosystems.

This research is focused on the identification of source chemicals; characterization of the chemical, physical, and biological processes acting on pollutants in the environment; and measurement of the constants for those chemical and microbiological processes that affect the fate and effects of specific toxic substances of concern. State-of-the-art mathematical models for assessing and managing environmental pollution problems are the major end products of this research.

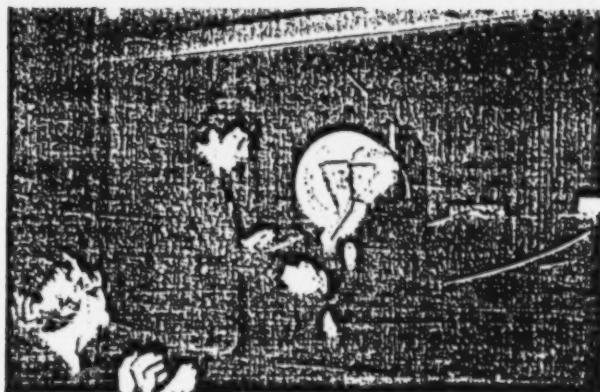
Vibrational spectroscopy is used to respond to this mission in two different types of applications. One area involves the identification of unlisted pollutants—a conventional, but somewhat specialized, usage of vibrational spectroscopy. The second area, a more novel application of vibrational spectroscopy and one for which few related studies have been reported, involves the prediction of environmental fate constants. For both areas, current and planned future work will be addressed here in an effort to give brief examples of how vibrational spec-

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The U.S. Environmental Protection Agency's Environmental Research Laboratory in Athens, Georgia



Dr. Bryce Crawford enlightens the audience at the Williams-Wright Symposium after being awarded honorary membership in the Coblentz Society.



Dr. Foil Miller (right) receives an honorary membership plaque from Coblenz Society President Rod McDowell, at the annual meeting held at the Pittsburgh Conference.

troscopy continues to contribute to environmental protection.

Identification of Unlisted Organic Pollutants with Vibrational Spectroscopy

Prerequisite to assessing risk posed by man-made chemicals to human health and the environment is the identification of pollutants, either in the ambient environment or in potential sources. With approximately eight million chemicals in the Chemical Abstracts Services Registry, the number of chemicals that can conceivably reach detectable concentrations in the ambient environment is very large. Since these compounds frequently are indistinguishable by chromatographic retention time data alone, identifications require more characteristic information. Because some chemicals cause adverse effects at low concentrations, measurement methods must be not only highly selective but also capable of achieving low levels of detection.

In the early 1970s, Drs. John McGuire, Lawrence Keith, and Arthur W. Garrison at the AERL demonstrated the applicability of GC/MS to the identification and measurement of trace organics in water. GC/MS rapidly became widely accepted as a reliable method for identifying and measuring trace organics in water, but mass spectra alone were not sufficiently distinguishing to ensure identification of all chemicals. To provide a manageable approach to the control of potentially harmful trace organics in water, EPA has developed lists of specific chemicals that would likely occur frequently (e.g., the List of Priority Pollutants and the Superfund Target Chemical List). These relatively few listed chemicals can be identified with little uncertainty when both their mass spectra and GC retention times are determined.

While control of listed chemicals usually results in abatement procedures that also control most unlisted chemicals as well, several problems of chemical identification still remain. With relatively few chemicals listed, it is not unusual for analysis of a waste sample to reveal one hundred or more compounds present at analytically significant concentrations, with few of the compounds on the target lists. Nearly all samples contain numerous unlisted chemicals. Therefore, lists of regulated chemi-

cals need to be upgraded continually to increase the probability of detection. In order that the lists can be upgraded, unlisted chemicals must be identified. Furthermore, there will always be situations for which regulatory decisions require more information than that offered by listed compounds alone.

Identification of unlisted chemicals is necessary not only for the ambient environment but also in laboratory studies of chemical and microbial transformation and in toxicity screening programs. In toxicity screening, various chemically-separated fractions of wastewaters are subjected to bioassay in order to identify causes of toxicity. Chemicals in the various fractions then must be identified.

Vibrational spectroscopy, specifically GC/FT-IR, is beginning to play an important role in the identification of unlisted pollutants. When unlisted compounds are tentatively identified by low-resolution electron impact mass spectroscopy, GC/FT-IR can provide confirmation, particularly if chromatographic retention times and mass and infrared spectra are compared with those of known compounds. Often, in the complementary use of MS and IR, one technique is strong where the other is deficient. For instance, distinguishing between positional isomers is often trivial with IR but virtually impossible with MS.

Perhaps the most important analytical role of vibrational spectroscopy in this application is for the identification of compounds that elude even tentative identification by low-resolution mass spectroscopy because their spectra are missing from computer libraries and application of mass fragmentation theory provides insufficient information. Multispectral techniques are used to elucidate structures for these compounds. Infrared spectroscopy provides substructural information from the presence, or absence, of characteristic group frequencies. High-resolution mass spectroscopy reduces the number of possible empirical formulae for each mass fragment, including the molecular ion if it is present, and chemical ionization mass spectroscopy identifies the molecular weight. Even when compounds are not uniquely identified, substructural information from IR spectra can provide insight into potential for toxicity or transformation. Since many potentially hazardous compounds are not amenable to solvent extraction and/or GC, LC/MS and LC/FT-IR must be considered in the future.

We believe that identification of the unlisted compounds present in ambient environmental samples would be of great benefit to any future efforts toward improved regulation. Additionally, identification of products and intermediates of chemical and microbial transformations is critical for understanding these processes. Spectral matching of solvent extraction-GC/MS data simply does not provide enough sample information to allow one to thoroughly characterize these samples. A multispectral identification approach, in which vibrational spectroscopy plays a significant role, offers the potential to do so.

Prediction of Environmental Fate Constants of Organic Chemicals with Vibrational Spectroscopy

Predictive risk assessment for hazardous chemicals is essential for implementing various provisions of the Tox-

ic Substance Control Act, the Resource Conservation and Recovery Act, Superfund, and the Clean Water Act. A prerequisite for predictive risk assessment is the knowledge of the transport and transformation of chemicals of concern in the environment. Therefore, each chemical's microbial and chemical transformation rate constants (as well as other physical and chemical characteristics) must be known. Reliable literature values for these process constants are not available for most chemicals, and due to the large number of chemicals of interest, required rate and equilibrium constants cannot always be measured in the laboratory in a timely and cost-efficient manner.

A novel application of vibrational spectroscopy currently underway at AERL involves the development of Property-Reactivity Correlations (PRCs) for the prediction of these environmental fate constants for organic chemicals, based on their spectroscopic properties. Such correlations (and subsequent predictions) are possible when the factors that affect specific vibrational band frequencies and/or intensities for a given functionality are the same factors that affect fate constants for compounds containing that functionality.

To apply this prediction method to a given class of compounds, one must identify some spectral feature of the parent structural unit, whose change will be consistent with the change in fate constants induced by the structural variations throughout the series. Once semi-empirical relationships are identified for a class of compounds, reliable estimates of fate constants can be made for other compounds in the class. With the wealth of information available in a vibrational spectrum, we are finding this possible for many situations. For example, since the microbially-mediated hydrolysis (biolysis) of certain secondary amides proceeds by cleavage of the amide linkage, and since the rate constant of the process (k_h) is dependent on the polar and steric nature of the substituents adjacent to that linkage, we have been able to correlate the frequencies of amide I and amide II IR peaks (which also depend on these polar and steric factors) with k_h for these compounds. An advantage of using spectral data as opposed to derived measures of polar or steric factors (e.g., Hammett constants or van der Waals radii, respectively) for these PRCs is that, if not found in a data compilation, the spectroscopic parameters can be measured in a rapid and precise manner.

The carbonyl vibration (which is the primary component of the amide I band) is, in fact, a good candidate for investigations of generalized PRCs for environmental fate constants, because many other compounds of environmental concern (esters, carboxylic acids, carbamates, ureas, anhydrides, etc.) degrade in natural waters by cleavage of bonds joining a carbonyl carbon to other atoms in the molecule. Spectroscopically, the carbonyl band is ideal for this work, for the same reasons that it is a good group frequency (i.e., has high absorptivity, occurs in an uncongested frequency region, provides definite assignments, exhibits sensitivity to surrounding environment). Other groups, such as P=O, P-O-R, R-O-R, R-NH₂, and R-OH—which are both environmentally important and, to a certain extent, good group frequencies—are also candidates for correlation. Currently, preliminary investigations are underway with both

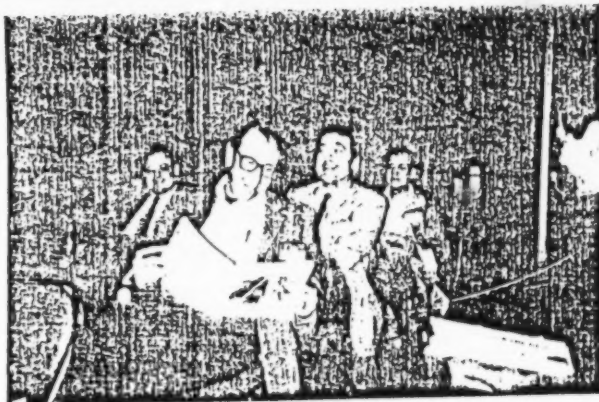


Dr. Bob Hannah (right) receives an award of appreciation from Colbentz Society President Rod McDowell, for 20 years of service as secretary of our organization. (Bob is laughing? Does anyone know why?)

substituted anilines and substituted phenols regarding the relationship between their IR spectra and their previously published rates of microbial oxidation. The parameters being considered in these investigations are derived from IR N-H and O-H stretching peaks, respectively. GC/FT-IR provides a convenient sampling method for these investigations because hydrogen bonding interferes with delineating the desired information in the condensed phase.

Another, somewhat more specialized, but nonetheless useful, approach to spectral-based PRCs has recently been applied to various alkyl esters of phthalic acid. Previous fate studies on these compounds by other workers have shown that as the hydrocarbon chain length increases, fate constants, [both k_h and the alkaline hydrolysis rate constant (k_{OH})] decrease. Furthermore, for a given number of carbon atoms in the alkyl chain, fate constants decrease markedly if the chain is branched. For all phthalate esters considered, including both normal- and branched-alkyl chains, excellent correlations of fate constants with parameters based on IR C-H vibrational peak intensities have been obtained for both k_h and k_{OH} . Once established, the PRCs were used to predict the k_h for two phthalate esters for which adequate literature values were not found. The correlations identified in this study indicated a generally applicable approach to spectral-based PRCs for other classes of compounds in which a variation in fate constants is observed for different hydrocarbon substituents. In order that this approach might be cultivated, the relationship between the IR spectra and the k_h 's for a series of alkyl esters of 2,4-D is currently under study.

All the work in spectral-based PRCs at AERL, to this point, has been done with IR spectroscopy. In certain cases, peak frequencies have been the best parameters for correlations, and in other cases, peak intensities. Each parameter has certain advantages, as well as disadvantages, for this application, in comparison to the other. Although peak frequencies are much easier to accurately measure, the variation of peak intensities throughout a series of compounds can be much greater. Due to the importance of vibrational peak intensities in these studies, plans are currently being made to incorporate Raman



Bruce Chase (front) enjoys (?) the Pittsburgh Conference program, as do (left to right, in the background) Barry Struesand, Rocky Carter, and Ira Levin.

spectral data, as this procedure may, in many cases, provide invaluable and unique information, since IR and Raman peak intensities depend on different physical qualities, yielding complementary information about the compound. Another important advantage of Raman spectroscopy for this work is the fact that, with this technique, vibrational spectra can be recorded in the same media in which the rate constants are determined (i.e., natural waters).

The purpose of the above discussion is to give a glimpse of two ways (one conventional and one novel) in which vibrational spectroscopy is playing a role in addressing environmental problems. If more information about the outlined projects, or citations of the published work discussed, is desired, please contact Dr. Tim Collette at EPA, College Station Road, Athens, GA 30613.

TIMOTHY W. COLLETTE

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